

02/14/00  
JC674 U.S. PTO

02-15-00

PATENT APPLICATION

A

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No. 11610US02

PATENT APPLICATION TRANSMITTAL

**Box Patent Application**  
**Assistant Commissioner for Patents**  
**Washington, D.C. 20231**

JC564 U.S. PTO  
09/503760  
02/14/00

Sir:

Transmitted herewith for filing is the patent application of

Inventor(s): Charles Stone and Alfred Eduard Steck

Title: GRAFT POLYMERIC MEMBRANES AND ION-EXCHANGE  
MEMBRANES FORMED THEREFROM

**1. Type of Application**

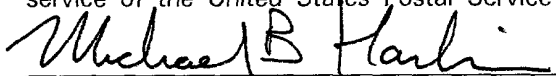
This application is a: continuation-in-part (CIP) of prior application  
Serial No. 08/967,960, filed November 12, 1997.

**2. Application Papers Enclosed**

- 1 Title Page
- 28 Pages of Specification (excluding Claims, Abstract & Drawings)
- 16 Page(s) of Claims
- 1 Page(s) of Abstract
- 2 Sheet(s) of Drawings (FIGs. 1 - 2) Informal

**CERTIFICATION UNDER 37 CFR 1.10**

I hereby certify that this Patent Application Transmittal and the documents referred to as enclosed therewith are being deposited with the United States Postal Service on February 14, 2000, in an envelope addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231 utilizing the "Express Mail Post Office to Addressee" service of the United States Postal Service under Mailing Label No. EL 026008430US

  
Michael B. Harlin

3. Declaration or Oath

Enclosed

Executed by (check all applicable boxes)

Inventor(s)

Legal representative of inventor(s)

(37 CFR 1.42 or 1.43)

Joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached

The petition required by 37 CFR 1.47 and the statement required by 37 CFR 1.47 are enclosed. See Item 5D below for fee.

☒ Not enclosed - the undersigned attorney or agent is authorized to file this application on behalf of the applicant(s). An executed declaration will follow.

4. Additional Papers Enclosed

Preliminary Amendment

Information Disclosure Statement, including copies of cited references

Declaration of Biological Deposit

Computer readable copy of sequence listing containing nucleotide and/or amino acid sequence

Verified statement(s) claiming small entity status under 37 CFR 1.9 and 1.27

Associate Power of Attorney

Verified translation of a non-English patent application

An assignment of the invention

Certified copy(ies) of application(s):

COUNTRY	APPLICATION NO.	FILED

from which priority under 35 USC 119 is claimed

is(are) attached.

will follow.

Other:

5. Filing Fee Calculation (37 CFR 1.16)

A. : Utility Application

CLAIMS AS FILED - INCLUDING PRELIMINARY AMENDMENT (IF ANY)						
			SMALL ENTITY		OTHER THAN A SMALL ENTITY	
	NO. FILED	NO. EXTRA	RATE	FEE	RATE	FEE
BASIC FEE				\$		\$ 690.00
TOTAL	71 - 20	= 51	X 9 =	\$	X 18 =	\$ 918.00
INDEP.	4 - 3	= 1	X 39 =	\$	X 78 =	\$ 39.00
First Presentation of Multiple Dependent Claim			+ 130 =	\$	+ 260 =	\$ 130.00
Filing Fee:				\$	<b>OR</b>	\$1,777.00

B. Design Application (\$155.00/\$310.00) Filing Fee: \$ \_\_\_\_\_

C. Plant Application (\$240.00/\$480.00) Filing Fee: \$ \_\_\_\_\_

D. Other Fees

Recording Assignment [Fee -- \$40.00 per assignment] \$ \_\_\_\_\_

Petition fee for filing by other than all the inventors  
or person on behalf of the inventor where inventor refused  
to sign or cannot be reached [Fee -- \$130.00] \$ \_\_\_\_\_

Other \$ \_\_\_\_\_

**Total Fees Enclosed \$ 1,777.00**

6. Method of Payment of Fees

Enclosed one (1) check in the amounts of: \$ \_\_\_\_\_

Charge Deposit Account No. 13-0017 in the amount of: \$ 1,777.00

Not enclosed

7. **Deposit Account and Refund Authorization**

The Commissioner is hereby authorized to charge any deficiency in the amount enclosed or any additional fees which may be required during the pendency of this application under 37 CFR 1.16 or 37 CFR 1.17 or under other applicable rules (except payment of issue fees), to Deposit Account No. 13-0017.

Please refund any overpayment to Deposit Account No. 13-0017.

Please direct all future communications to Robert W. Fieseler at the address and telephone number below.

McAndrews, Held & Malloy, Ltd.  
500 West Madison Street, 34th Floor  
Chicago, Illinois 60661

(312) 775-8000

Please direct all telephone calls to Robert W. Fieseler at (312) 775-8123. Please direct all facsimile transmissions to Robert W. Fieseler at (312) 775-8100. Please direct all e-mail transmissions to rfieseler@mhmllaw.com.

Respectfully submitted,

By: Michael B. Harlin  
Robert W. Fieseler  
Registration No. 31,826  
Michael B. Harlin  
Registration No. 43,658

Date: February 14, 2000

**GRAFT POLYMERIC MEMBRANES AND  
ION-EXCHANGE MEMBRANES FORMED THEREFROM**

**Cross-Reference to Related Application**

This is a continuation-in-part of application Serial No. 08/967,960 filed on November 12, 1997, entitled "Graft Polymeric  
5 Membranes and Ion-Exchange Membranes Formed Therefrom". The '960 application, incorporated herein by reference in its entirety, describes polymeric compositions comprising a polymeric base film to which has been radiation grafted one  
10 or more of a variety of substituted trifluorovinyl aromatic monomers. These compositions are suitable for use as membranes, particularly as ion-exchange membranes.

15

**Field Of The Invention**

The present invention relates to graft polymeric membranes in which one or more trifluorovinyl aromatic monomers are radiation  
20 graft polymerized to a polymeric base film, and methods for making same wherein the grafted polymeric chains are modified to incorporate ion-exchange groups. The resultant membranes are useful in dialysis applications, and particularly  
25 in electrochemical applications, for example as membrane electrolytes in electrochemical fuel cells and electrolyzers.

### Background Of The Invention

The preparation of graft polymeric membranes by radiation grafting of a monomer to a polymeric base film has been demonstrated for various combinations of monomers and base films. The grafting of styrene to a polymeric base film, and subsequent sulfonation of the grafted polystyrene chains has been used to prepare ion-exchange membranes.

U.S. Patent No. 4,012,303 reports the radiation grafting of  $\alpha,\beta,\beta$ -trifluorostyrene (TFS) to polymeric base films using gamma ray co-irradiation, followed by the introduction of various ion-exchange substituents to the pendant aromatic rings of the grafted chains. With co-irradiation, since the TFS monomer is simultaneously irradiated, undesirable processes such as monomer dimerization and/or independent homopolymerization of the monomer may occur in competition with the desired graft polymerization reaction.

U.S. Patent No. 4,012,303 also reports that the TFS monomer may be first sulfonated and then grafted to the base film. Thus, the introduction of ion-exchange groups into the membrane can be done as part of the grafting process, or in a second step.

More recently, the grafting of TFS to pre-irradiated polymeric base films, followed by the

introduction of various substituents to the pendant aromatic rings of the grafted chain has been reported in U.S. Patent No. 4,605,685.

5 Solid or porous polymeric base films, such as for example polyethylene and polytetrafluoroethylene, are pre-irradiated and then contacted with TFS neat or in solution. Pre-irradiation is reportedly a more economic and efficient grafting technique, reportedly giving a percentage graft  
10 of 10-50% in reaction times of 1-50 hours. Aromatic sulfonation, haloalkylation, amination, hydroxylation, carboxylation, phosphonation and phosphorylation are among the reactions subsequently used to introduce ion-exchange  
15 groups into the grafted polymeric chains. Levels of post-sulfonation from 40% to 100% are reported.

In either case the prior art TFS-based grafted membranes incorporate statistically a  
20 maximum of one functional group per monomer unit in the grafted chain. Further, they typically incorporate only one type of functional group as substituents on the pendant aromatic rings in the grafted chains.

25 In the present membranes, one or more types of substituted TFS monomers and/or substituted  $\alpha,\beta,\beta$ -trifluorovinyl naphthylene (TFN) monomers are grafted to polymeric base films, the substituents being selected to offer particular advantages,  
30 for example:

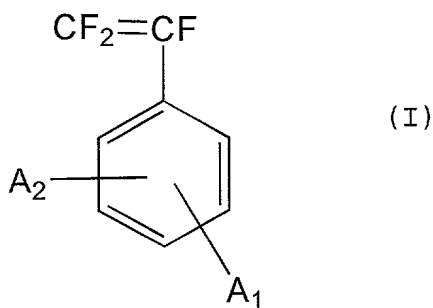
- 5 (a) Substituted TFS and/or TFN monomers that are activated have increased reactivity in the grafting reaction facilitating graft polymerization. By "activated" it is meant that either the percentage graft yield of the graft polymerization reaction is increased, or that the rate of the reaction is increased, in reactions employing the substituted monomers relative to reactions employing unsubstituted monomers.
- 10 (b) Substituted TFS and/or TFN monomers in which the substituents are activating with respect to the grafting reaction, but which can be converted so as to be de-activating with respect to subsequent reactions to introduce, for example, ion-exchange functionality into the grafted chains, and thereby permit the introduction of ion-exchange groups that are more stable under certain conditions.
- 15 (c) Substituted TFS and/or TFN monomers in which the substituents are activating with respect to the grafting reaction, but which can be converted so as to be de-activating after introduction of ion-exchange functionality into the grafted chains.
- 20
- 25
- 30



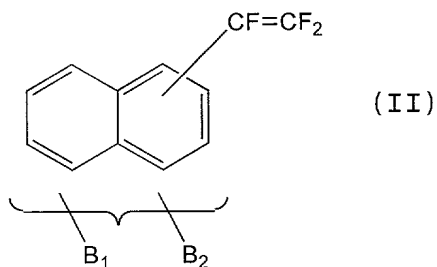
- (d) Grafted chains comprising monomer units with more than one aromatic ring permit the introduction of more than one ion-exchange group per grafted monomer unit, enabling the achievement of higher ion-exchange capacities at lower percentage grafts than in prior art grafted polymeric membranes.
- (e) Substituted TFS and/or TFN monomers in which the substituents are precursors to ion-exchange groups may be transformed to ion-exchange groups after the grafting reaction, and can facilitate the introduction of more than one type of ion-exchange group into the grafted chains, for example, so that both cation and anion-exchange groups may be incorporated in a membrane.
- (f) Substituted TFS and/or TFN monomers in which the substituents contain functionality that can be further reacted to allow for the preparation of crosslinked graft polymeric membranes that may display, for example, greater dimensional stability under certain conditions than similar graft polymeric membranes that are not crosslinked.

### Summary Of The Invention

A graft polymeric membrane is provided in which one or more types of trifluorovinyl aromatic monomers are graft polymerized to a  
5 polymeric base film. In some embodiments, the membrane comprises a polymeric base film to which has been graft polymerized a monomer (meaning at least one type of monomer) selected from the group consisting of monomers of the following  
10 formulae (I) and (II):



and



where  $A_1$ ,  $A_2$ , and  $B_1$ ,  $B_2$  are independently selected from the group consisting of hydrogen, lower alkyl, lower fluoroalkyl, cyclic alkyl, cyclic  
30 amine, cyclic ether, cyclic thioether, aryl

(provided that where one of  $A_1$  and  $A_2$  is hydrogen, aryl is other than Ph, wherein Ph is phenyl),  $CH(X)Ph$  (where X is selected from the group consisting of hydrogen, fluorine, lower alkyl, lower fluoroalkyl and Ph),  $PRR'$  and  $P(OR)(OR')$  (where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different); and, wherein  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$  can be the same or different, provided that in the selected monomer at least one of the substituents  $A_1$ ,  $A_2$ ,  $B_1$ ,  $B_2$  is other than hydrogen. In other words there is at least one of the substituent on foregoing monomers used in the graft polymerization reaction. The selected substituted monomer(s) may have one or two non-hydrogen substituents.

Of the listed alkyl substituents, lower alkyl and cyclic alkyl are generally preferred, with methyl (Me) being most preferred. Thus, membranes where one or both substituents on the selected monomer of formula (I) or (II) are Me are particularly preferred (with para-Me being the most desirable substitution positions in formula (I)). In these embodiments the base film preferably comprises poly(ethylene-co-tetrafluoroethylene).

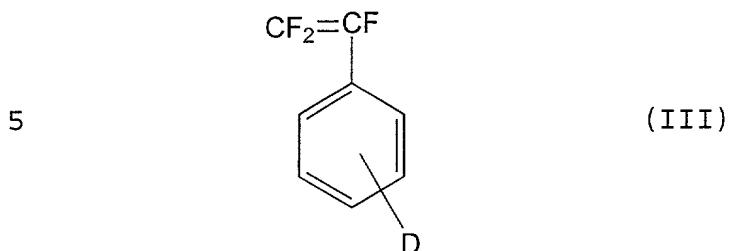
In embodiments in which a polymeric base film has been graft polymerized with a monomer of

formula (I) in which  $A_1$  is aryl and  $A_2$  is hydrogen, the aryl is preferably a fused polycyclic aromatic with two fused rings, biphenyl, or a heteroaromatic group with at least one heteroatom which is preferably nitrogen, oxygen or sulfur. If the heteroaromatic group contains more than one heteroatom, the heteroatoms may be the same or different. If one of the heteroatoms is nitrogen it may be advantageously N-alkylated or N-benzylated for certain membrane applications. Monocyclic heteroaromatics are generally preferred over polycyclic heteroaromatics.

The above graft polymeric membrane may comprise a single monomer, whereby the grafted chains are homopolymeric, or may comprise more than one monomer such that the grafted chains are copolymeric. For example, the graft polymeric membrane may comprise more than one monomer of formula (I) having different  $A_1$  and/or  $A_2$  substituents, more than one monomer of formula (II) having different  $B_1$  and/or  $B_2$  substituents, more than one monomer of either formula (I) or formula (II) having the same substituents located at different positions, or monomers of both formula (I) and (II), such that the grafted chains are copolymeric.

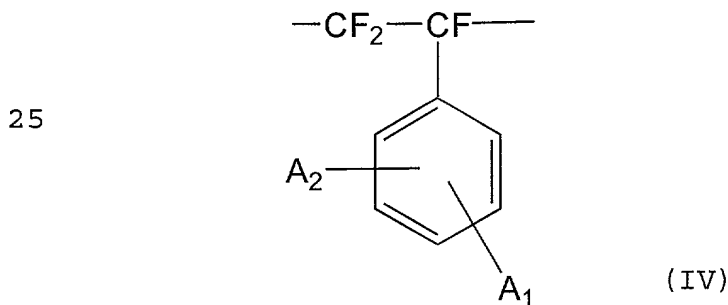
In other embodiments of the present graft polymeric membrane, the membrane comprises a polymeric base film to which has been graft

polymerized, with the foregoing monomers, a monomer of the following formula (III):

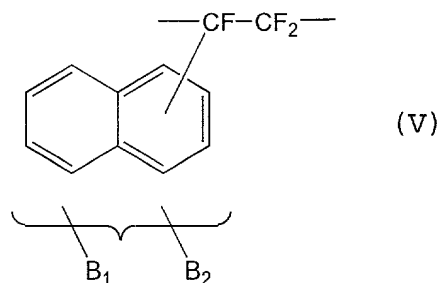


where D is selected from the group consisting of hydrogen, fluorine,  $\text{CF}_3$ ,  $\text{CF}_2\text{H}$ ,  $\text{CF}=\text{CF}_2$ ,  $\text{SO}_2\text{F}$  and  $\text{SO}_3^-\text{M}^+$  where  $\text{M}^+$  is a suitable counterion, such as, for example, metal cations and quaternary ammonium ions.

Embodiments of the present graft polymeric membrane may comprise a polymeric base film with grafted chains comprising monomer units selected from the group consisting of monomer units of the following formulae (IV) and (V), wherein at least a portion of the monomer units further optionally comprise at least one ion-exchange substituent, in which case the membrane is an ion-exchange membrane:



30 and



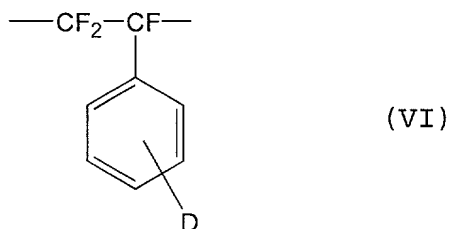
5

where, as before,  $A_1$ ,  $A_2$ , and  $B_1$ ,  $B_2$  are independently selected from the group consisting of hydrogen, lower alkyl, lower fluoroalkyl, cyclic alkyl, cyclic amine, cyclic ether, cyclic thioether, aryl (provided that where one of  $A_1$  and  $A_2$  is hydrogen, aryl is other than Ph, wherein Ph is phenyl),  $CH(X)Ph$  (where X is selected from the group consisting of hydrogen, fluorine, lower alkyl, lower fluoroalkyl and Ph),  $PRR'$  and  $P(OR)(OR')$  (where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different); and wherein  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$  can be the same or different, provided that at least one of the substituents  $A_1$ ,  $A_2$  is other than hydrogen. The foregoing membranes may be formed by grafting monomers to a polymeric base film, or by grafting to some other form of polymeric substrate and then forming the grafted material into a membrane. In some embodiments of the ion-exchange membranes, statistically at least 50% of the monomer units in the grafted chains have at least one ion-exchange substituent

per monomer unit. In other embodiments at least a portion of the monomer units comprise more than one ion-exchange substituent, and/or portion of the grafted chains may comprise at least two  
 5 different types of ion-exchange groups, which may even include both anion and cation exchange groups. The ion-exchange substituent most typically incorporated is a sulfonate or sulfonic acid group.

10 In preferred embodiments one or both substituents of the monomer units of formulae (IV) or (V) are  $\text{CH}(\text{X})\text{Ph}$  (where X is selected from the smaller group consisting of hydrogen, fluorine, Me and Ph), or Me, with para-Me being  
 15 the most desirable substitution position for the Me group in units of formula (IV). In these embodiments, again, the base film preferably comprises poly(ethylene-co-tetrafluoroethylene).

The grafted chains of ion-exchange membrane  
 20 may further comprise additional monomer units, such as for example, units of formula (VI):



25 where D is selected from the group consisting of hydrogen, fluorine,  $\text{CF}_3$ ,  $\text{CF}_2\text{H}$ ,  $\text{CF}=\text{CF}_2$ ,  $\text{SO}_2\text{F}$  and  
 30  $\text{SO}_3^-\text{M}^+$  where  $\text{M}^+$  is a suitable counterion.

The ion-exchange membrane may be substantially gas impermeable. Such gas impermeable ion-exchange membranes may be incorporated into an electrode apparatus such as,  
5 for example, a membrane electrode assembly. Electrochemical fuel cells that comprise such ion-exchange membranes are also provided. For fuel cell applications, the polymeric base film of the ion-exchange membrane is preferably less  
10 than 100  $\mu\text{m}$  thick.

In the present graft polymeric membranes or ion-exchange membranes, at least a portion of the grafted chains may be crosslinked.

Other membranes may be prepared from those  
15 membranes described above by subjecting them to a reaction process selected from the group consisting of, halomethylation, sulfonation, phosphonation, amination, carboxylation, hydroxylation and nitration. These are non-  
20 limiting but preferred examples of reaction processes; other reaction processes may also be used. Membranes so prepared may be useful ion-exchange membranes or precursors to ion-exchange membranes. Methods of preparing the present  
25 membranes and ion-exchange membranes are also contemplated and described herein.

Ion-exchange membranes may be prepared by a method which comprises graft polymerizing to a polymeric base film a monomer selected from the  
30 group consisting of monomers of formulae (I) and



(II) described above, wherein in the selected monomer(s) at least one of the substituents  $A_1$ ,  $A_2$ , and  $B_1$ ,  $B_2$  is a non-hydrogen substituent which activates the monomer with respect to graft  
5 polymerization (relative to the corresponding unsubstituted monomer). The method further comprises introducing a sulfonate group (or other ion-exchange group) into at least a portion of the graft polymerized monomer units and  
10 converting at least a portion of the non-hydrogen substituents to substituents which are deactivating with respect to desulfonation (relative to the unsubstituted monomer unit). The conversion of the non-hydrogen substituent to  
15 a deactivating group may be performed before or after introduction of the sulfonate group into the grafted units.

Some of the membranes described above may be prepared by a method comprising graft  
20 polymerizing to a polymeric base film a substituted monomer selected from the group consisting of monomers of formulae (I) and (II) described above, wherein  $A_1$ ,  $A_2$ , and  $B_1$ ,  $B_2$  are as described above.

25 In preferred embodiments of this method,  $A_1$  and  $B_1$  are independently selected from the group consisting of:

aryl (where aryl is selected from the group consisting of monocyclic  
30 heteroaromatics, fused polycyclic

heteroaromatics, and heteroaromatic ring assemblies having at least one nitrogen atom);

cyclic amine; and

5 phosphines of the formula  $PRR'$  and phosphites of formula  $P(OR)(OR')$  (where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or  
10 different); and

$A_2$  and  $B_2$  are hydrogen.

The method further comprises alkylating or benzylating at least a portion of any of the nitrogen atoms of the aryl group, the nitrogen  
15 atoms of the cyclic amine, or the phosphorus atoms of the phosphine or phosphite.

In other embodiments where  $A_1$  and  $B_1$  are independently selected from the group consisting of phosphines of the formula  $PRR'$  and phosphites  
20 of formula  $P(OR)(OR')$  (where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different), and  $A_2$  and  $B_2$  are hydrogen, the method may further comprise the  
25 sequential steps of introducing a nitro group into at least a portion of the monomer units of the membrane and converting at least a portion of those nitro groups to quaternary ammonium groups. This method optionally further comprises

subsequently converting said phosphine or phosphite to an ion-exchange substituent.

In still another embodiment, the present method comprises graft polymerizing to a

5 polymeric base film a monomer selected from the group consisting of monomers of the formulae (I) and (II) described above, but where  $A_1$  and  $B_1$  are independently selected from the group consisting of  $PRR'$ ,  $P(OR)(OR')$ , and  $SR$  (where  $R$  and  $R'$  are

10 independently selected from the group consisting of lower alkyl, cyclic alkyl and  $Ph$ , and where  $R$  and  $R'$  can be the same or different), and  $A_2$  and  $B_2$  are the same as  $A_1$  and  $B_1$  respectively or hydrogen. The method comprises the steps of

15 graft polymerizing the monomers to a polymeric base film, and oxidizing at least a portion of the  $PRR'$ ,  $P(OR)(OR')$ , or  $SR$  groups to produce phosphine oxides, phosphones, phosphonates, sulfoxides, or sulfones. The method may further

20 comprise introducing ion-exchange substituents into at least a portion of said monomer units, before or after the oxidation step. Where  $A_1$  and  $B_1$  are independently selected from the group  $SR$  (where  $R$  is selected from the group consisting of

25 lower alkyl, cyclic alkyl and  $Ph$ ), and  $A_2$  and  $B_2$  are the same as  $A_1$  and  $B_1$  respectively or hydrogen, the method optionally further comprises converting at least a portion of the  $SR$  groups to sulfonate or sulfonic acid groups.

In the above-described embodiments the substrate for the graft polymerization is preferably a polymeric base film. However, the polymeric substrate may be in other forms such as, for example, a powder or in solution, or the substrate may be an oligomer in any suitable form. Where the substrate is not in the form of a film an additional step will be required to form the grafted material into a membrane. Where the substrate is in solution an additional solvent removal step will be required.

#### **Brief Description Of The Drawings**

FIG. 1 is a plot of cell voltage as a function of current density (expressed in mA/cm<sup>2</sup>) in an electrochemical fuel cell employing a sulfonated membrane of p-Me-TFS grafted poly(ethylene-co-tetrafluoroethylene) and operating on hydrogen-oxygen (plot A) and hydrogen-air (plot B).

FIG. 2 is a plot of cell voltage as a function of current density (expressed in mA/cm<sup>2</sup>) in an electrochemical direct methanol fuel cell employing a sulfonated membrane of p-Me-TFS grafted poly(ethylene-co-tetrafluoroethylene) operating on aqueous methanol-air.

#### **Detailed Description Of Preferred Embodiment(s)**

As used in this description and in the appended claims, in relation to substituents of

TFS and/or TFN monomers, lower alkyl means straight chain or branched C<sub>1</sub> - C<sub>6</sub> alkyl groups. Lower fluoroalkyl means partially or completely fluorinated straight or branched C<sub>1</sub> - C<sub>6</sub> saturated chains, provided that the benzylic carbon has no more than one fluorine atom attached thereto. In preferred embodiments, the lower alkyl and lower fluoroalkyl are C<sub>1</sub> - C<sub>4</sub>. Other haloalkyls of the same general description may also be used in connection with the present membranes, however, fluorine is preferred due to the relative lability of chlorine, bromine and iodine to substitution, which may result in competition in other reaction processes or in undesirable side reactions. Cyclic alkyl means cyclic alkyls having C<sub>3</sub> - C<sub>7</sub> rings. Cyclic amine means nonaromatic heterocyclic 2° or 3° amines having 3-7 atoms in the ring (for example, piperidine, piperazine, and quinuclidene). Cyclic ether means nonaromatic heterocyclic ethers having 3-7 atoms in the ring (for example, tetrahydrofuran and dioxane). Cyclic thioether means nonaromatic heterocyclic thioethers having 3-7 atoms in the ring (for example, tetrahydrothiophene and dithiane). Aryl means: monocyclic aromatic rings; fused polycyclic hydrocarbons containing at least one aromatic ring (for example, indan); fused polycyclic aromatic hydrocarbons (for example, indene and naphthalene); aromatic ring assemblies (for example, biphenyl); and, heteroaromatics

thereof, wherein the heteroatoms are nitrogen, oxygen, or sulfur, and the heterocyclic may contain more than one heteroatom, and may also contain different species of heteroatom (for  
5 example, indoline, pyrrole, pyridine, oxathiazine, and purine). The abbreviation Me is used to represent a methyl group, and the abbreviation Ph is used to represent a phenyl group. The formula  $\text{SO}_3^-\text{M}^+$  represents sulfonate  
10 salts, where  $\text{M}^+$  may be any suitable counterion, such as, for example, metal cations and quaternary ammonium ions.

Suitable substituents for TFS and/or TFN monomers that are activating in graft  
15 polymerization reactions include, for example: lower alkyls; lower fluoroalkyls; cyclic alkyls; cyclic amines; cyclic ethers; cyclic thioethers; aryl groups; and, phosphines, phosphites, and thioethers. Substituents may be coupled to the  
20 aromatic rings of TFS and/or TFN monomers in any suitable position. Meta- and para-substituted monomers are preferred, with para-substituted monomers being more preferred.

Any suitable radiation capable of  
25 introducing sufficient concentrations of free radical sites on and within the base polymeric film may be used in the preparation of the grafted polymeric membranes described herein. For example, the irradiation may be by gamma  
30 rays, X-rays, electron beam, or high-energy UV

radiation. Electron beam irradiation is generally preferable as the process times are short and thus more suited to high volume production processes. The decay of the source and typically longer reactions times required with gamma-ray radiation tend to render it less suitable for high volume manufacturing processes.

The polymeric base film may be pre-irradiated prior to bringing it into contact with the monomer or monomer mixture to be grafted or the substrate and monomer(s) may be irradiated together (co-irradiation).

For the preparation of membranes, grafting to a polymeric base film is generally more efficient and cost-effective than grafting to a substrate in some other form such as a powder and then forming a membrane from the grafted material.

The preferred polymeric base film material is dependent on the application in which the grafted membrane is to be used. The base film may be a porous or dense film. Preferred substrate materials for electrochemical applications, for example, include hydrocarbons such as polyolefins, especially polyethylene and polypropylene. In some applications, a perfluorinated or partially fluorinated polymeric base film may be used, for example, polytetrafluoroethylene (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene),

polyvinylidene fluoride, and preferably  
poly(ethylene-co-tetrafluoroethylene).

In the grafting reaction, the polymeric base  
film is treated with the monomer(s) in the liquid  
5 phase, either as a neat liquid or in a solution.  
Alternatively, the polymeric base film may be  
treated with a mixture of liquid and vapor phase  
monomer(s) (including aerosols), or with  
monomer(s) in the vapor phase only. It can be  
10 advantageous to select a solvent that will cause  
the solution to penetrate the base film and cause  
it to swell. This facilitates grafting of the  
monomer(s) throughout the membrane thickness.  
Preferably the irradiation and grafting process  
15 is carried out in an inert atmosphere.

The reaction conditions may be selected so  
as to introduce crosslinking between monomer  
units during graft polymerization or subsequent  
thereto. Crosslinking may be introduced into  
20 polymeric membranes where it is, for example,  
desirable to increase dimensional stability,  
reduce swelling, modify chemical and/or  
mechanical properties, or enhance the ion-  
exchange efficiency. Methods of preparing  
25 crosslinked graft polymeric membranes are known  
in the art. For example, U.S. Patent No.  
5,656,386 describes adding a crosslinking agent  
to vinyl monomers to be grafted to a membrane  
film, wherein the radiation grafting and  
30 crosslinking reactions occur simultaneously.



In the present graft polymeric membranes, the constituent monomers may be selected so as to be capable of forming crosslinks without requiring the addition of a separate crosslinking agent. If crosslinking is desirable, the monomer(s) preferably contains functionality that can be crosslinked. For example, monomers having a t-butyl group as a substituent would be less appropriate, since such substituents do not participate readily in crosslinking reactions. As another example, monomers having  $-\text{CHF}_2$  or  $-\text{CH}(\text{CF}_3)_2$  substituents are capable of forming very stable crosslinks, but such monomers may be so de-activating towards polymerization that the percentage graft or rate of grafting may fall to an undesirable level. However, such monomers may be suitably used in the grafting reaction provided they are included in the monomer mixture at a relatively low mole percentage (for example, less than about 10 mol%).

For the preparation of grafted ion-exchange membranes from substituted TFS and/or TFN monomers, substituents that are activating with respect to the polymerization reaction are typically also activating towards subsequent reactions to introduce ion-exchange groups, such as, for example, halomethylation, sulfonation, phosphonation, amination, carboxylation, hydroxylation (optionally combined with subsequent phosphorylation) and nitration.

Although the presence of an activating  
substituent may be beneficial in that it may  
facilitate the introduction of the ion-exchange  
group into the monomer, where the ion-exchange  
5 group is sulfonate, for example, there may also  
be a disadvantage. This is because sulfonation  
is a macroscopically reversible process, so a  
substituent that is activating with respect to  
the introduction of a sulfonate group may also  
10 make the sulfonate group less stable under  
certain conditions, thereby facilitating  
desulfonation of the monomer unit.

In some embodiments of the present membranes  
or method, the substituted TFS and/or TFN  
15 monomers to be grafted contain a phosphine,  
phosphite, or thioether substituent. These  
substituents are activating with respect to the  
graft polymerization reaction. Ion-exchange  
groups such as, for example, sulfonate, may then  
20 be introduced into the aromatic ring of the  
substituted TFS and/or TFN monomer units after  
graft polymerization. Then, following graft  
polymerization the phosphine, phosphite or  
thioether groups can be oxidized to produce  
25 phosphine oxides, phosphones, phosphonates,  
sulfoxides, or sulfones. Methods suitable for  
such oxidations are well known to those skilled  
in the art. The resulting phosphine oxides,  
phosphones, phosphonates, sulfoxides and/or  
30 sulfones are de-activating, thus making the

introduced ion-exchange groups, in particular sulfonate groups, more stable under certain conditions.

In addition, these substituents may allow  
5 for the introduction of additional ion-exchange  
functionality into the TFS and/or TFN monomer  
units. For example, oxidation of the phosphite  
substituent yields a phosphonate group, which on  
hydrolysis will yield a cation-exchange group.  
10 Introduction of either cation or anion-exchange  
groups into the substituted TFS and/or TFN  
monomer units, followed by oxidation of phosphite  
and subsequent hydrolysis of the phosphonate  
substituent, may yield TFS and/or TFN monomer  
15 units with more than one ion-exchange group per  
monomer unit, on average. As another example,  
the phosphine or phosphite substituent may be  
alkylated or benzylated to form an anion-exchange  
group. Further, employing the additional steps  
20 of nitration followed by conversion of the nitro  
group to an amino group, and subsequently to a  
quaternary ammonium salt may yield monomer units  
having two different anion-exchange groups. As  
yet another example, the thioether substituent  
25 may be converted to a sulfonate group by, for  
example, the method described in U.S. Patent No.  
5,830,962. Again, introduction of either cation  
or anion-exchange groups into the substituted TFS  
and/or TFN monomer units, followed by alkylation  
30 or benzylation of the phosphine, or conversion of

thioether to sulfonate, may yield TFS and/or TFN monomer units with more than one ion-exchange group per monomer, on average, depending upon the compatibility of the chemistry involved. Thus, the present method allows for the preparation of amphoteric graft ion-exchange membranes, or graft ion-exchange membranes having two different ion-exchange groups, simply by choosing the appropriate ion-exchange group to be introduced into the substituted TFS and/or TFN monomer units.

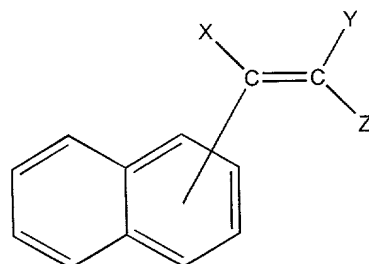
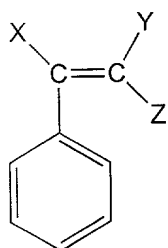
In another embodiment of the present membranes and method, the substituted TFS and/or TFN monomers to be grafted contain a cyclic 2° or 3° amine or a heteroaromatic substituent containing at least one nitrogen heteroatom. These substituents are also activating with respect to the graft polymerization reaction. Following graft polymerization, the cyclic amine or heteroaromatic substituents can be N-alkylated or N-benzylated, forming anion-exchange sites in the grafted chains. Optionally, cation-exchange groups may also be introduced, either before or preferably after N-alkylation or N-benylation, resulting in amphoteric ion-exchange membranes.

In the foregoing embodiments of the present membranes and method, sulfonate ion-exchange groups can be introduced to the monomer units in the grafted chains. For example, the membrane,

preferably swollen with an appropriate solvent to facilitate sulfonation throughout its thickness, can be reacted with a solution of sulfur trioxide, or with sulfur trioxide vapor alone (or indeed an aerosol mist of sulfur trioxide). Other sulfonation reagents can be used, as will be familiar to those skilled in the art, such as oleum and chlorosulfonic acid, for example.

While the foregoing methods have been described in relation to substituted TFS and/or TFN monomers, it will be readily apparent to those skilled in the art that the foregoing methods are readily adaptable to other monomers. It is anticipated that other vinyl monomers containing an aromatic ring may be suitably adaptable to the disclosed methods. For example, in the preparation of graft membranes employing styrenic monomers, it would still be advantageous to employ substituents that are activating with respect to the graft polymerization reaction, but which can be converted to de-activating substituents in subsequent reactions where it is desirable to introduce, for example, ion-exchange groups that may, by this process, be more stable under certain conditions. In addition to styrenic monomers, it is expected that the foregoing methods will be adaptable to substituted and unsubstituted monomers of the following basic structures:

5



- 10 where X can be H, F or Me and  
 if X = F, then Y = Z = H, or one of Y, Z is H and  
 the other is F,  
 if X = H, then Y = Z = H, or one of Y, Z is H and  
 the other is F, and  
 15 if X = Me, then Y = Z = H.

The following examples are for purposes of  
 illustration and are not intended to limit the  
 invention.

20

#### EXAMPLE 1

25 **Grafting of para-methyl- $\alpha,\beta,\beta$ -trifluorostyrene  
 (p-Me-TFS) to poly(ethylene-co-  
tetrafluoroethylene) (Tefzel®) Film**

A 2 mil (approx. 50  $\mu\text{m}$ ) thick, 7 inch  $\times$  7  
 inch (18 cm  $\times$  18 cm) piece of poly(ethylene-co-  
 30 tetrafluoroethylene) (Tefzel®) film was

irradiated with a dose of 20 Mrad using a high energy electron beam (60 kW) radiation source, in an inert atmosphere. The irradiated base film was kept at -30°C in an inert atmosphere prior to use. The irradiated membrane was then exposed to neat, degassed p-Me-TFS in an inert atmosphere at 80°C for 24 hours. The p-Me-TFS grafted film was removed, washed with toluene and dried at 60°C. The percentage graft was 79%. In these Examples, the percentage graft is the increase in weight of the film after the grafting reaction compared to the weight of the film before the grafting reaction.

## EXAMPLE 2

### Grafting of para-methyl- $\alpha,\beta,\beta$ -trifluorostyrene (p-Me-TFS) to poly(ethylene-co-tetrafluoroethylene) (Tefzel®) Film

A 2 mil (approx. 50  $\mu$ m) thick, 15 inch  $\times$  15 inch (38 cm  $\times$  38 cm) piece of poly (ethylene-co-tetrafluoroethylene) (Tefzel®) film was irradiated with a dose of 20 Mrad using a high energy electron beam (60 kW) radiation source, in an inert atmosphere. The irradiated base film was stored at -30°C in an inert atmosphere prior to use. The irradiated membrane was then exposed to neat, degassed p-Me-TFS in an inert atmosphere at 70°C for 3 hours. The p-Me-TFS grafted film

was removed, washed with toluene and dried at 60°C. The percentage graft was 67%.

5

### EXAMPLE 3

**Grafting of para-methyl- $\alpha,\beta,\beta$ -trifluorostyrene  
(p-Me-TFS) to poly(ethylene-co-  
tetrafluoroethylene) (Tefzel®) Film and  
Sulfonation of the Grafted Membrane**

10

(a) A 2 mil (approx. 50  $\mu$ m) thick, 7 inch x 7 inch (18 cm x 18 cm) piece of poly(ethylene-co-tetrafluoroethylene) (Tefzel®) film was irradiated with a dose of 10 Mrad using a high energy electron beam (60 kW) radiation source, in an inert atmosphere. The irradiated base film was kept at -30°C in an inert atmosphere prior to use. It was then exposed to neat, degassed, p-Me-TFS in an inert atmosphere at 50°C for 60 hours. The p-Me-TFS grafted film was removed, washed with toluene and dried at 60°C. The percentage graft was 49%.

(b) A sulfonating solution was prepared by careful addition of 30 g of liquid sulfur trioxide to 70 g of 1,1,2,2-tetrachloroethane. The grafted membrane was sulfonated by immersion in the above-mentioned sulfonating solution for 2 hours at 70°C. The resultant ion-exchange



membrane was washed with water and dried at 60°C. The equivalent weight of the sulfonated membrane was 660 g/mol, with a water content of 26% at room temperature.

5

#### EXAMPLE 4

Grafting of para-methyl- $\alpha,\beta,\beta$ -trifluorostyrene  
(p-Me-TFS) to poly(ethylene-co-  
tetrafluoroethylene) (Tefzel®) Film and  
10 Sulfonation of the Grafted Membrane

(a) A 2 mil (approx. 50  $\mu$ m) thick, 7 inch x 7  
inch (18 cm x 18 cm) piece of poly(ethylene-co-  
tetrafluoroethylene) (Tefzel®) film was grafted  
15 with para-methyl- $\alpha,\beta,\beta$ -trifluorostyrene similarly  
as in Example 3, using a 5 Mrad irradiation dose.  
The percentage graft was 35%.

(b) The grafted film was sulfonated according to  
20 the procedure described in step (b) of Example 3.  
The equivalent weight of the sulfonated membrane  
was 821 g/mol, with a water content of 18% at  
room temperature.

25

# EXAMPLE 5

## Use of Sulfonated p-Me-TFS grafted poly(ethylene-co-tetrafluoroethylene) Membrane as an Ion-exchange Membrane in a Fuel Cell

5

The membrane prepared as described in Example 3 was bonded to two catalyzed carbon fiber paper electrodes to form a membrane electrode assembly having a total platinum catalyst loading of 1 mg/cm<sup>2</sup>. The membrane electrode assembly was tested in a Ballard Mark IV single cell fuel cell. The following operating conditions were used:

15

Temperature: 80°C

Reactant inlet pressure:

3.02 bara for oxidant and fuel

Reactant stoichiometries:

2.0 oxidant and 1.5 hydrogen.

20

FIG. 1 shows polarization plots of voltage as a function of current density for the sulfonated grafted membrane employed in a membrane electrode assembly in the electrochemical fuel cell operating on hydrogen-oxygen (plot A) and hydrogen-air (plot B).

25

# EXAMPLE 6

## Use of Sulfonated p-Me-TFS grafted poly(ethylene-co-tetrafluoroethylene) Membrane as an Ion-exchange Membrane in a Fuel Cell

5

The membrane prepared as described in Example 4 was bonded to two catalyzed carbon fiber paper electrodes to form a membrane electrode assembly having a total platinum  
10 catalyst loading of 8 mg/cm<sup>2</sup>. The membrane electrode assembly was tested in a Ballard Mark IV single cell direct methanol fuel cell. The following operating conditions were used:

15       Temperature: 110°C;  
          Fuel: 0.4 M methanol solution (in water);  
          Reactant inlet pressure: 3.02 bara for  
          oxidant and fuel;  
          Reactant stoichiometries: 2.0 oxidant and  
20       3.0 methanol.

FIG. 2 shows polarization plots of voltage as a function of current density for the sulfonated grafted membrane employed in a  
25 membrane electrode assembly in the electrochemical fuel cell operating on methanol-air.

In addition to the utility of the grafted membranes described herein in ion exchange  
30 membranes for electrochemical fuel cells, it is

contemplated that such membranes will also have utility in the following applications:

- (1) as membranes in filtration and ultrafiltration applications;
- 5 (2) as proton exchange membranes in water electrolysis, which involves a reverse chemical reaction to that employed in hydrogen/oxygen electrochemical fuel cells;
- 10 (3) as membranes in chloralkali Electrolysis, which typically involves the electrolysis of a brine solution to produce chlorine and sodium hydroxide, with hydrogen as a by-
- 15 product;
- (4) as electrode separators in conventional batteries, provided the membrane has the requisite chemical inertness and high electrical conductivity;
- 20 (5) as ion-selective electrodes, particularly those used for the potentiometric determination of a specific ion such as  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and like ions;
- 25 (6) as sensor materials for humidity sensors based on ion exchange membranes, as the electrical conductivity of an ion exchange membrane varies with humidity;

- 5 (7) as ion exchange membranes for separations by ion exchange chromatography - typical such applications are deionization and desalination of water, ion separations, removal of interfering ionic species, and separation and purification of biomolecules;
- 10 (8) as ion exchange membranes employed in analytical pre- concentration techniques (for example, Donnan Dialysis);
- 15 (9) as ion exchange membranes in electrodialysis, in which membranes are employed to separate components of an ionic solution under the driving force of an electrical current - industrial applications include desalination of brackish water, preparation of boiler feed make-up and chemical process water, de-ashing of sugar solutions, deacidification of citrus juices, separation of amino acids, and the like;
- 20 (10) as membranes in dialysis applications, in which solutes diffuse from one side of the membrane (the feed side) to the other side according to their concentration gradient - applications
- 25

include haemodialysis and the  
removal of alcohol from beer;

(11) as membranes in gas separation (gas  
permeation) and pervaporation (liquid  
permeation) techniques; and

5

(12) as bipolar membranes employed in water  
splitting and subsequently in the  
recovery of acids and bases from waste  
water solutions.

10

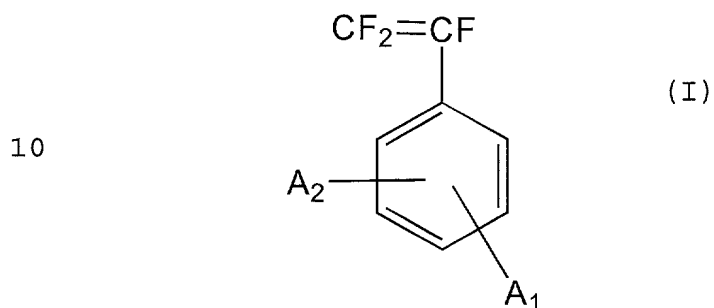
While particular elements, embodiments and  
applications of the present invention have been  
shown and described, it will be understood, of  
course, that the invention is not limited thereto  
since modifications may be made by those skilled  
in the art, particularly in light of the  
foregoing teachings. It is therefore  
contemplated by the appended claims to cover such  
modifications as incorporate those features which  
come within the spirit and scope of the  
invention.

15

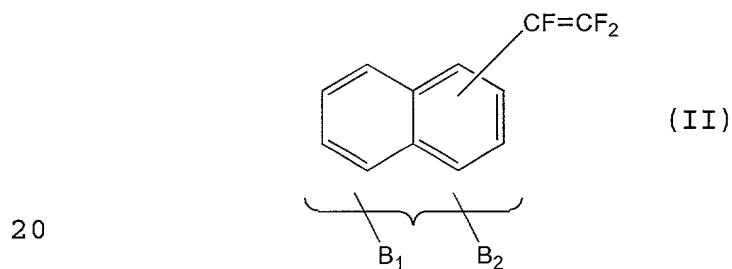
20

What is claimed is:

1. A membrane comprising a polymeric base film to which has been graft polymerized a monomer selected from the group consisting of monomers of formula (I)



15 and formula (II)



25 where  $A_1$ ,  $A_2$ , and  $B_1$ ,  $B_2$  are independently selected from the group consisting of:

hydrogen, lower alkyl, lower fluoroalkyl, cyclic alkyl, cyclic amine, cyclic ether, cyclic thioether,

aryl, provided that where one of  $A_1$  and  $A_2$  is hydrogen, aryl is other than Ph, wherein Ph is phenyl,

5 CH(X)Ph, where X is selected from the group consisting of hydrogen, fluorine, lower alkyl, lower fluoroalkyl and Ph,

PRR' and P(OR)(OR'), where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and  
10 Ph, and where R and R' can be the same or different, and

wherein  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$  can be the same or different, provided that in each monomer, at least one of the substituents  $A_1$ ,  
15  $A_2$ ,  $B_1$ ,  $B_2$  is other than hydrogen.

2. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I),  
20 wherein  $A_1$  is other than hydrogen, and  $A_2$  is hydrogen.

3. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I),  
25 wherein  $A_1$  and  $A_2$  are other than hydrogen.

4. A membrane according to claim 1 comprising a polymeric base film to which has



been graft polymerized a monomer of formula (II) wherein  $B_1$  is other than hydrogen, and  $B_2$  is hydrogen.

5            5.    A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (II), wherein  $B_1$  and  $B_2$  are other than hydrogen.

10           6.    A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I) wherein  $A_1$  is selected from the group consisting of lower alkyl and cyclic alkyl, and  $A_2$  is the  
15    same as  $A_1$  or hydrogen.

             7.    A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (II)  
20    wherein  $B_1$  is selected from the group consisting of lower alkyl and cyclic alkyl, and  $B_2$  is the same as  $B_1$  or hydrogen.

             8.    A membrane according to claim 1  
25    comprising a polymeric base film to which has been graft polymerized a monomer of formula (I) wherein  $A_1$  is selected from the group consisting of cyclic amine, cyclic ether, cyclic thioether, and wherein  $A_2$  is hydrogen.

9. A membrane according to claim 1  
comprising a polymeric base film to which has  
been graft polymerized a monomer of formula (I)  
wherein A<sub>1</sub> is selected from the group consisting  
5 of aryl groups, and wherein A<sub>2</sub> is hydrogen.

10. A membrane according to claim 9,  
wherein said aryl group is a fused polycyclic  
aromatic with two fused rings.

10

11. A membrane according to claim 9,  
wherein said aryl group is biphenyl.

12. A membrane according to claim 9,  
15 wherein said aryl group is a heteroaromatic  
group.

13. A membrane according to claim 12,  
wherein said aryl group is a heteroaromatic group  
20 containing at least one heteroatom, wherein said  
at least one heteroatom is selected from the  
group consisting of nitrogen, oxygen and sulfur.

14. A membrane according to claim 13,  
25 wherein said heteroaromatic group contains at  
least two of said heteroatoms, and said  
heteroatoms can be the same or different.

15. A membrane according to claim 13,  
wherein at least one of said heteroatoms is  
nitrogen which is N-alkylated or N-benzylated.

5        16. A membrane according to claim 13,  
wherein said heteroaromatic group is monocyclic.

10        17. A membrane according to claim 1  
comprising a polymeric base film to which has  
been graft polymerized a monomer of formula (I)  
wherein  $A_1$  is selected from the group consisting  
of  $PRR'$  and  $P(OR)(OR')$ , where R and R' are  
independently selected from the group consisting  
of lower alkyl, cyclic alkyl and Ph, and where R  
15 and R' can be the same or different, and wherein  
 $A_2$  is hydrogen.

20        18. A membrane according to claim 1  
comprising a polymeric base film to which has  
been graft polymerized a monomer of formula (I)  
wherein  $A_1$  is selected from the group consisting  
of Me and  $CH(X)Ph$ , where X is selected from the  
group consisting of hydrogen, fluorine, Me, and  
Ph, and  $A_2$  is the same as  $A_1$  or hydrogen.

25

19. A membrane according to claim 1  
comprising a polymeric base film to which has  
been graft polymerized a monomer of formula (II)  
wherein  $B_1$  is selected from the group consisting

of Me and CH(X)Ph, where X is selected from the group consisting of hydrogen, fluorine, Me and Ph, and B<sub>2</sub> is hydrogen.

5           20. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I) wherein A<sub>1</sub> is Me and A<sub>2</sub> is Me or hydrogen.

10           21. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (II) wherein B<sub>1</sub> is Me and B<sub>2</sub> is Me or hydrogen.

15           22. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I) wherein A<sub>1</sub> is para-Me, A<sub>2</sub> is hydrogen, and said base film comprises poly(ethylene-co-  
20 tetrafluoroethylene).

            23. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (II)  
25 wherein B<sub>1</sub> is Me, B<sub>2</sub> is hydrogen, and said base film comprises poly(ethylene-co-tetrafluoroethylene).

            24. A membrane according to claim 1  
30 comprising a polymeric base film to which has

been graft polymerized one monomer selected from the group consisting of said monomers of formula (I) and formula (II), whereby the grafted chains are homopolymeric.

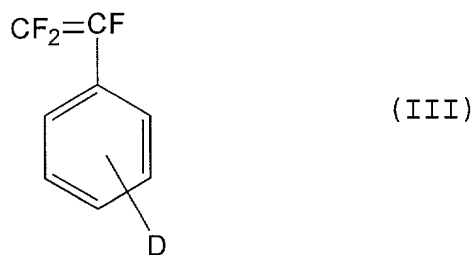
5

25. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized more than one monomer selected from the group consisting of said  
10 monomers of formula (I) and formula (II), whereby said grafted chains are copolymeric.

26. A membrane according to claim 1 comprising a polymeric base film to which has  
15 been graft polymerized more than one monomer of formula (I), whereby the grafted chains are copolymeric.

27. A membrane according to claim 1  
20 comprising a polymeric base film to which has been graft polymerized more than one monomer of formula (II), whereby the grafted chains are copolymeric.

28. A membrane according to claim 1  
25 comprising a polymeric base film to which has been graft polymerized a monomer of formula (III) in addition to said monomers selected from the group consisting of monomers of formula (I) and  
30 formula (II):



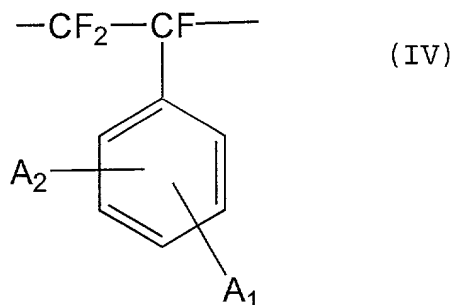
5

where D is selected from the group consisting of hydrogen, fluorine,  $\text{CF}_3$ ,  $\text{CF}_2\text{H}$ ,  $\text{CF}=\text{CF}_2$ ,  $\text{SO}_2\text{F}$  and  $\text{SO}_3^-\text{M}^+$  where  $\text{M}^+$  is a suitable counterion.

10

29. A membrane comprising a polymeric base film with grafted chains comprising monomer units selected from the group consisting of monomer units of formula (IV)

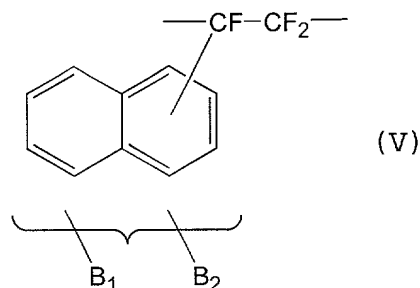
15



20

and formula (V)

25



30

where  $A_1$ ,  $A_2$ , and  $B_1$ ,  $B_2$  are independently  
5 selected from the group consisting of:

hydrogen, lower alkyl, lower  
fluoroalkyl, cyclic alkyl,  
cyclic amine, cyclic ether, cyclic  
thioether,

10 aryl provided that where one of  $A_1$  and  
 $A_2$  is hydrogen, aryl is other than Ph,

CH(X)Ph, where X is selected from the  
group consisting of hydrogen, fluorine,  
lower alkyl, lower fluoroalkyl and Ph,  
15 wherein Ph is phenyl,

PRR' and P(OR)(OR') where R and R' are  
independently selected from the group  
consisting of lower alkyl, cyclic alkyl and  
Ph, and where R and R' can be the same or  
20 different,

and wherein  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$  can be the same  
or different, provided that in each of said  
monomer units at least one of the substituents  $A_1$ ,  
 $A_2$ ,  $B_1$ ,  $B_2$  is other than hydrogen.

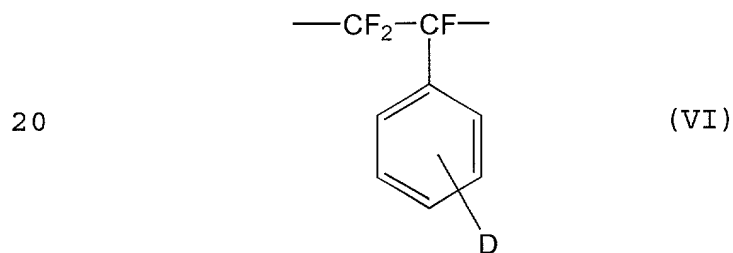
25

30. A membrane according to any one of  
claims 1, 20-23, 28 or 29 wherein at least a  
portion of the grafted chains are crosslinked.

31. A membrane according to claim 29  
wherein at least a portion of said monomer units  
further comprise at least one ion-exchange  
substituent, whereby said membrane is an ion-  
5 exchange membrane.

32. An ion-exchange membrane according to  
claim 31 wherein said at least one ion-exchange  
substituent is a sulfonate or sulfonic acid  
10 substituent.

33. An ion-exchange membrane according to  
claim 31 comprising a polymeric base film with  
grafted chains further comprising monomer units  
15 of formula (VI) in addition to said monomer units  
selected from the group consisting of monomer  
units of formula (IV) and formula (V):



where D is selected from the group  
25 consisting of hydrogen, fluorine,  $\text{CF}_3$ ,  $\text{CF}_2\text{H}$ ,  
 $\text{CF}=\text{CF}_2$ ,  $\text{SO}_2\text{F}$  and  $\text{SO}_3^-\text{M}^+$  wherein  $\text{M}^+$  is a suitable  
counterion.

34. An ion-exchange membrane according to  
30 claim 31 wherein at least a portion of said



monomer units comprise at least two ion-exchange substituents.

35. An ion-exchange membrane according to  
5 claim 31 wherein at least 50% of said monomer units in said grafted chains have at least one ion-exchange substituent per monomer unit.

36. An ion-exchange membrane according to  
10 claim 31 wherein said grafted chains comprise at least two different types of ion-exchange groups.

37. An ion-exchange membrane according to  
15 claim 31 wherein said grafted chains comprise an anion-exchange group and a cation-exchange group.

38. An ion-exchange membrane according to  
any one of claims 31 or 33 wherein at least a portion of the grafted chains are crosslinked.  
20

39. An ion-exchange membrane according to claim 31 wherein said ion-exchange membrane is substantially gas impermeable.

25 40. An ion-exchange membrane according to claim 32 wherein said ion-exchange membrane is substantially gas impermeable.

41. An ion-exchange membrane according to claim 31 wherein said monomer units are of formula (IV).

5           42. An ion-exchange membrane according to claim 41 wherein  $A_1$  is selected from the group consisting of Me and  $CH(X)Ph$ , where X is selected from the group consisting of hydrogen, fluorine, Me and Ph, and  $A_2$  is the same as  $A_1$  or hydrogen

10           43. An ion-exchange membrane according to claim 41 wherein  $A_1$  is Me and  $A_2$  is Me or hydrogen.

15           44. An ion-exchange membrane according to claim 41 wherein  $A_1$  is para-Me,  $A_2$  is hydrogen, said base film comprises poly(ethylene-co-tetrafluoroethylene), and said at least one ion-exchange substituent is a sulfonate or sulfonic  
20 acid group.

          45. An ion-exchange membrane according to claim 31 wherein said monomer units are of formula (V).

25           46. An ion-exchange membrane according to claim 45 wherein  $B_1$  is selected from the group consisting of Me and  $CH(X)Ph$ , where X is selected from the group consisting of hydrogen, fluorine,  
30 Me and Ph, and  $B_2$  is hydrogen.

47. An ion-exchange membrane according to claim 45 wherein  $B_1$  is Me and  $B_2$  is Me or hydrogen.

5

48. An ion-exchange membrane according to claim 45 wherein  $B_1$  is Me,  $B_2$  is hydrogen, said base film comprises poly(ethylene-co-tetrafluoroethylene), and said at least one ion-exchange substituent is a sulfonate or sulfonic acid group.

10

49. An electrode apparatus comprising an ion-exchange membrane of claim 39.

15

50. An electrode apparatus comprising an ion-exchange membrane of claim 40.

51. A membrane electrode assembly comprising an ion-exchange membrane of claim 39.

20

52. A membrane electrode assembly comprising an ion-exchange membrane of claim 40.

53. An electrochemical fuel cell comprising an ion-exchange membrane of claim 39.

25

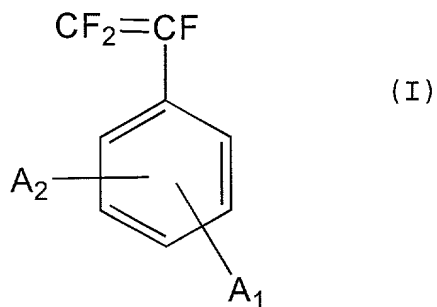
54. An electrochemical fuel cell comprising an ion-exchange membrane of claim 40.

30

55. An electrochemical fuel cell according to any one of claims 53 or 54 wherein said polymeric base film is less than 100  $\mu\text{m}$  thick.

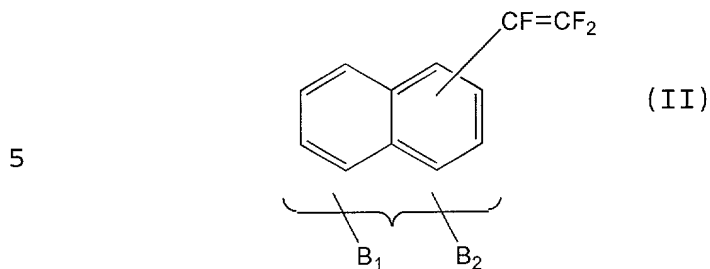
5 56. A membrane prepared by subjecting a membrane of claim 1 to a reaction process selected from the group consisting of halomethylation, sulfonation, phosphonation, amination, carboxylation, hydroxylation and  
10 nitration.

57. A method of preparing a membrane, said method comprising graft polymerizing to a polymeric base film a monomer selected from the  
15 group consisting of monomers of formula (I)



20

and formula (II)



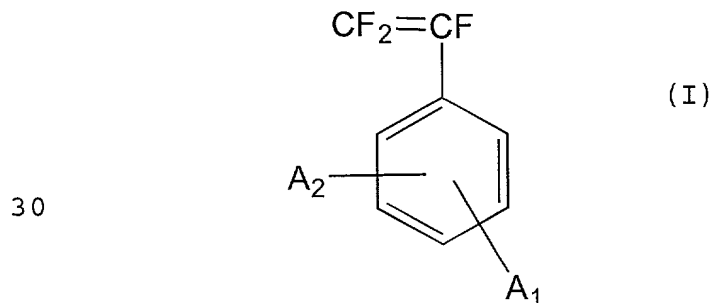
wherein in the selected monomer at  
 10 least one of  $A_1$ ,  $A_2$ , and at least one of  $B_1$ ,  $B_2$  is  
 a substituent other than hydrogen which activates  
 said monomer with respect to said graft  
 polymerizing, and said method further comprises:

introducing a sulfonate group into at least  
 15 a portion of said graft polymerized monomer  
 units; and

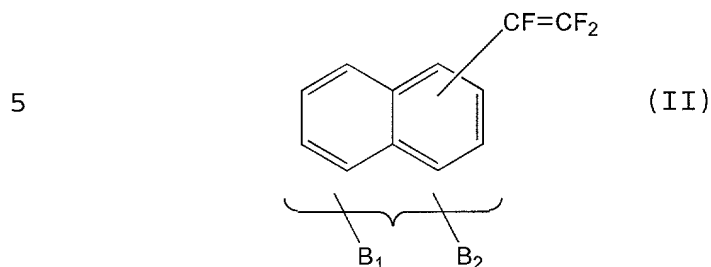
converting at least a portion of said  
 substituent to substituent which are deactivating  
 with respect to desulfonation.

20

58. A method of preparing a membrane, said  
 method comprising graft polymerizing to a  
 polymeric base film a monomer selected from the  
 25 group consisting of monomers of formula (I)



and formula (II)



10        where  $A_1$ ,  $A_2$ , and  $B_1$ ,  $B_2$  are independently  
selected from the group consisting of:

hydrogen, lower alkyl, lower fluoroalkyl,  
cyclic alkyl, cyclic amine, cyclic ether, cyclic  
thioether,

15        aryl, provided that where one of  $A_1$  and  $A_2$  is  
hydrogen, aryl is other than Ph, wherein Ph is  
phenyl,

CH(X)Ph, where X is selected from the group  
consisting of hydrogen, fluorine, lower alkyl,  
20    lower fluoroalkyl and Ph,

PRR' and P(OR)(OR') (where R and R' are  
independently selected from the group consisting  
of lower alkyl, cyclic alkyl and Ph, and where R  
and R' can be the same or different, and

25        wherein  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$  can be the same or  
different, provided that in each monomer at least  
one of the substituents  $A_1$ ,  $A_2$ ,  $B_1$ ,  $B_2$  is other  
than hydrogen.

59. A method according to claim 58, wherein  $A_1$  and  $B_1$  are independently selected from the group consisting of

an aryl group selected from the group  
5 consisting of monocyclic heteroaromatics, fused  
polycyclic heteroaromatics, and heteroaromatic  
ring assemblies having at least one nitrogen  
atom,  
cyclic amine, and  
10 phosphines of the formula  $PRR'$  and phosphites  
of formula  $P(OR)(OR')$  where R and R' are  
independently selected from the group consisting  
of lower alkyl, cyclic alkyl and Ph, wherein Ph  
in phenyl, and where R and R' can be the same or  
15 different, and

$A_2$  and  $B_2$  are hydrogen,  
the method further comprising alkylating or  
benzylating at least a portion of any of said  
nitrogen atoms of said aryl group, the nitrogen  
20 atoms of said cyclic amine, or the phosphorus  
atoms of said phosphine or phosphite.

60. A method according to claim 58, wherein  $A_1$  and  $B_1$  are independently selected from the  
25 group consisting of

phosphines of the formula  $PRR'$  and phosphites  
of formula  $P(OR)(OR')$  where R and R' are  
independently selected from the group consisting

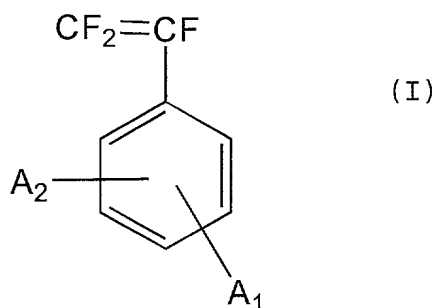
of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different, and

A<sub>2</sub> and B<sub>2</sub> are hydrogen,

the method comprising the sequential steps  
5 of introducing a nitro group into at least a portion of the grafted monomer units of said membrane and converting at least a portion of said nitro groups to quaternary ammonium groups,

the method optionally further comprising  
10 converting said phosphine or phosphite to an ion-exchange substituent.

61. A method of preparing a membrane  
comprising graft polymerizing to a polymeric base  
15 film a monomer selected from the group consisting of monomers of formula (I)

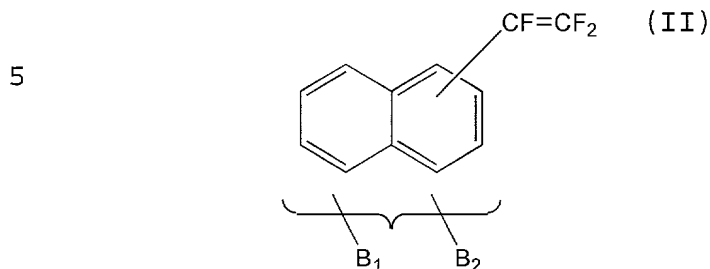


20

25



and formula (II)



10

where A<sub>1</sub> and B<sub>1</sub> are independently selected from the group consisting of

PRR', P(OR)(OR'), and SR where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different, and

15

A<sub>2</sub> and B<sub>2</sub> are the same as A<sub>1</sub> and B<sub>1</sub> respectively or hydrogen,

20

the method further comprising oxidizing at least a portion of the PRR', P(OR)(OR'), or SR groups.

62. The method of claim 61 further comprising introducing ion-exchange substituents into at least a portion of said monomer units.

25

63. The method of claim 61, wherein A<sub>1</sub> and B<sub>1</sub> are independently selected from the group SR,

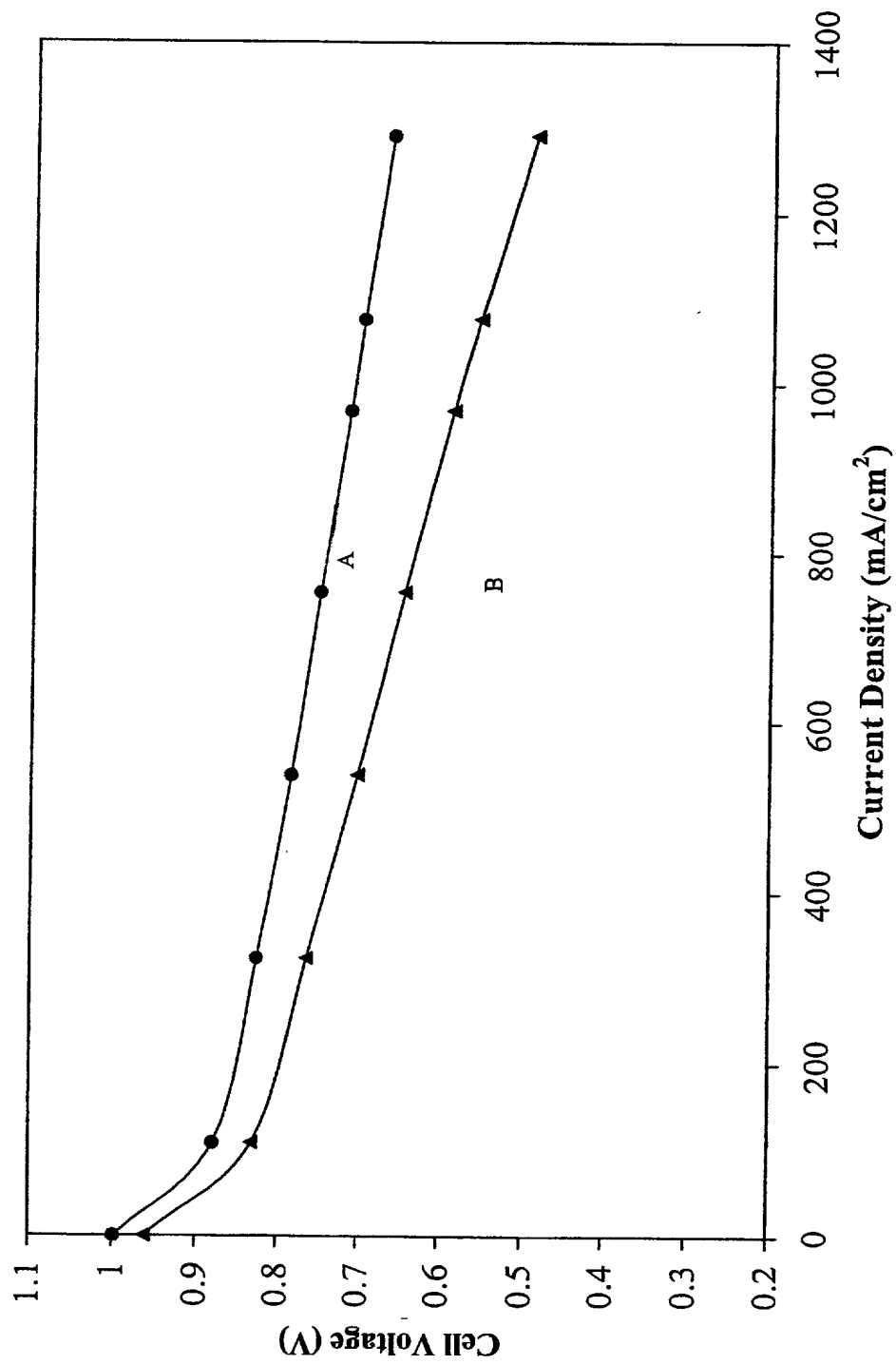
where R is selected from the group consisting of lower alkyl, cyclic alkyl and Ph, wherein Ph is phenyl, and A<sub>2</sub> and B<sub>2</sub> are the same as A<sub>1</sub> and B<sub>1</sub> respectively or hydrogen, and wherein the method comprises converting at least a portion of the SR groups to sulfonate or sulfonic acid groups.

**GRAFT POLYMERIC MEMBRANES AND  
ION-EXCHANGE MEMBRANES FORMED THEREFROM**

**Abstract**

Graft polymeric membranes and methods for making same are provided in which one or more trifluorovinyl aromatic monomers are radiation graft polymerized to a polymeric base film. The membranes comprise a polymeric base film to which has been graft polymerized substituted  $\alpha,\alpha,\beta$ -trifluorostyrene and/or  $\alpha,\alpha,\beta$ -trifluorovinyl-naphthylene monomers which are activated towards graft polymerization. The membranes may be ion-exchange membranes suitable for use in electrode apparatus, including membrane electrode assemblies that may be used in, for example, fuel cells. The membranes may be crosslinked.

**FIG. 1**



**FIG. 2**

